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Doppler-Free Resonances of the Second-Order Raman Scattering

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Abstract. The possibility of the observation of Raman scattering resonances completely free from the influence of the Doppler effect has been examined for the first time. The phenomenon is based on the excitation of a Raman oscillation standing wave in a gas by two standing light waves, whose frequency difference is equal to half the Raman frequency. The complete compensation of Doppler shifts results from the simultaneous interactions between atomic particles and two pairs of counter-propagating waves. Doppler-free resonances of the second-order Raman light scattering appear in the number of particles excited to the upper Raman level and in the radiation at the Stokes and anti-Stokes frequencies. The amplitude estimate for the resonance in the number of particles is given for the example of neon.

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The IR, FIR and millimeter quantum transitions can be effectively investigated by the laser spectroscopic methods of stimulated Raman scattering (SRS) and coherent anti-Stokes Raman scattering (CARS). These are vibrational and rotational molecular transitions, atomic transitions between fine structure levels and Rydberg states. The methods are based on the resonances arising if the frequency difference $\omega_1 - \omega_2$ of two light waves is equal to the quantum transition frequency ω_{eg}. The excitation of Raman oscillations at the frequency of the two-photon transition $g \rightarrow e$ is a linear process for each optical field interacting with the medium. Hence the resolution of SRS and CARS methods is very strongly influenced by the Doppler effect which results in Raman scattering anisotropy and defines the resonance width, which is of the same order as the optically allowed transition width [1]. The elimination of Doppler broadening in the case of a single-frequency optical field is known to occur if the atom–field interaction is strongly nonlinear, i.e., each interaction process simultaneously involves two counter-propagating photons [2] (see also the review [3]).

To eliminate the influence of the Doppler effect on the excitation of Raman oscillations, we suggest the realization of the two-photon interaction with each of the optical fields of two lasers at frequencies ω_1 and ω_2. This light scattering has to occur in the field of two standing light waves. It will have a resonance nature if twice the difference of laser frequencies $2(\omega_1 - \omega_2)$ approaches the frequency ω_{eg} of the atomic transition $g \rightarrow e$ between states of the same parity. We may consider this interaction as second-order stimulated Raman scattering, because the Raman coherence is proportional to the second power of each light field.

In comparison with two-photon resonances of SRS and CARS, the present four-photon resonance is completely free of any linear Doppler effect, and its linewidth is equal to the optically forbidden transition width. Four-photon Raman resonances have been observed in a condensed medium [4], but if the experimental method [4] based on the interaction with propagating light waves is applied in a gas, the resonance width is of the same order of magnitude as in the two-photon Raman case because Doppler broadening is not completely eliminated.

There are two mechanisms of Doppler-free interactions that contribute to the resonance excitation of the Raman oscillations ϱ_{eg} of the medium. The first is double SRS (Fig. 1a). The difference frequency Doppler shift $(\mp)$ $(\mathbf{k}_1-\mathbf{k}_2)\mathbf{v}$ acquired in the first SRS atomic interaction with copropagating waves at ω_1 and ω_2 is completely compensated by the shift $(\pm)$ $(\mathbf{k}_1-\mathbf{k}_2)\mathbf{v}$ in the second SRS interaction with mirror-reflected light waves. The latter interaction is synchronous with the first one. The other mechanism (Fig. 1b) involves two Doppler-free processes: stimulated two-photon absorption of the counterpropagating waves at frequency ω_1, and simultaneously, stimulated emission of two oppositely directed photons at frequency ω_2. The absence of the Doppler effect for this excitation of ϱ_{eg} is due to its absence in each elementary step.

The quantitative treatment of the coherence excitation by two standing light waves with the difference frequency $\omega_1-\omega_2$ close to the half of the Raman frequency $\omega_{eg}/2$ is given in Sect. 1.

The Doppler-free resonances may be observed in the number of particles excited to the upper Raman level and also in the radiation at Stokes and anti-Stokes frequencies (Sect. 2).

Since four photons are involved in each stage of the Raman coherence excitation, the process is essentially nonlinear and can occur only in strong optical fields. The question is what laser radiation intensities are required. The answer is given in Sect. 3, where, as an example, estimates are presented for the transition $^3P_2^0-{}^3P_0^0$ (776.8 cm^{-1}) in neon.

1. Resonance Excitation of the Doppler-Free Raman Oscillations

Let the atomic or molecular gas interact with the field of two standing electromagnetic waves

$$\mathbf{E}(z,t)=\sum_{j=1,2} 2E_j\boldsymbol{\varepsilon}_j\cos k_j z \times\exp(-\mathrm{i}\omega_j t)+\mathrm{c.c.}, \tag{1}$$

where $2E_j$, $\boldsymbol{\varepsilon}_j$, ω_j, k_j are the amplitude, polarization, frequency and wave number, respectively, for each of the propagating waves forming the standing wave.

The Raman oscillations of the medium at frequency ω_{eg} of the transition between the metastable states g and e (g may be the ground state) will be described by means of a nondiagonal element ϱ_{eg} of the density matrix. The amplitude of Raman oscillations is proportional to the squared product of the optical wave amplitudes, i.e., the resonance in ϱ_{eg} occurs in the fourth order of the field. The system of equations for the density matrix elements was solved according to the perturbation theory in the resonance approximation taking into account in the coherence ϱ_{eg} and upper level population ϱ_e only the interactions with the counter-propagating waves.

We find the steady state value

$$\varrho_{eg}=4\mathrm{i}(E_1E_2^*)^2\varrho_g\exp[-\mathrm{i}2(\omega_1-\omega_2)t]r_{eg},$$

where ϱ_g is the lower level population, and

$$r_{eg}=Q_{eg}[\Gamma-\mathrm{i}(\Omega+\Delta\omega)]^{-1},$$

where $\Omega=2(\omega_1-\omega_2)-\omega_{eg}$; Γ is the homogeneous halfwidth of the $g\to e$ transition, $\Delta\omega$ is the Stark shift in the optical field (1) of the two standing waves. The four-photon matrix element Q_{eg} and the light shift $\Delta\omega$ have been calculated, but now we shall confine ourselves to the approximate formula for Q_{eg} which may be used in the resonance amplitude estimation, and we shall omit $\Delta\omega$ which may be taken in order of magnitude from [3, 5] by analogy with the Doppler-free two-photon resonance. Thus,

$$Q_{eg}=Q_{eg}(\boldsymbol{\varepsilon}_2^*,\omega_2|\omega_1,\boldsymbol{\varepsilon}_1)\cdot +Q_{eg}(\boldsymbol{\varepsilon}_1,-\omega_1|-\omega_2,\boldsymbol{\varepsilon}_2^*), \tag{2}$$

$$Q_{eg}(\boldsymbol{\varepsilon}_2^*,\omega_2|\omega_1,\boldsymbol{\varepsilon}_1) \sim\sum_{\eta\neq g,e} D_{e\eta}(\boldsymbol{\varepsilon}_2^*,\omega_2|\boldsymbol{\varepsilon}_1)D_{\eta g}(\boldsymbol{\varepsilon}_2^*|\omega_1,\boldsymbol{\varepsilon}_1) \times[\omega_{\eta g}-(\omega_{eg}/2)]^{-1} +D_{e\eta}(\boldsymbol{\varepsilon}_2^*,\omega_2|\boldsymbol{\varepsilon}_2^*)D_{\eta g}(\boldsymbol{\varepsilon}_1|\omega_1,\boldsymbol{\varepsilon}_1)(\omega_{\eta g}-2\omega_1)^{-1}, \tag{3}$$

where the two-photon matrix elements are

$$D_{ba}(\boldsymbol{\varepsilon}_i,\omega|\boldsymbol{\varepsilon}_k)=\sum_\alpha\frac{\langle b|\boldsymbol{\varepsilon}_i\mathbf{d}|\alpha\rangle\langle\alpha|\boldsymbol{\varepsilon}_k\mathbf{d}|a\rangle}{\hbar^2(\omega_{\alpha b}-\omega)},$$

$$D_{ba}(\boldsymbol{\varepsilon}_i|\omega,\boldsymbol{\varepsilon}_k)=D_{ba}(\boldsymbol{\varepsilon}_i,\omega+\omega_{ab}|\boldsymbol{\varepsilon}_k),$$

where $\mathbf{d}$ is an atomic dipole moment.

The second item in (2) is obtained from the first one by the substitution of parameters and is taken into account in the case of the excitation through the intermediate levels α, β lying below the g, e levels. The relation between the left and right parts of (3) may be considered close to an equality when there exists a level η lying between g and e approximately in the middle or at a distance of two optical quanta from the g level ($|\omega_{\eta g}-\omega|\ll\omega_{eg}$; $\omega=\omega_{eg}/2$, $2\omega_1$).

In conclusion, we may add that the Doppler-free Raman oscillations do not depend on the coordinate z. Hence, one may consider them to be a standing wave.

2. Doppler-Free Resonances in the Number of Particles and in the Radiation

The upper level population resulting from the resonance Doppler-free four-photon interaction is pro-

portional to the eighth power of the field $\varrho_e \sim |E_1 E_2|^4$. The number of particles excited to the e state per time unit, averaged over velocities and coordinates is $\dot{N}_e = \gamma_e \int d\mathbf{v} d\mathbf{r} \varrho_e$, where γ_e is the relaxaton constant of the e state. We obtain

$$\dot{N}_e = 32 N_g |E_1 E_2|^4 S_{eg} Q_{eg}^* \Gamma (\Gamma^2 + \Omega^2)^{-1}. \quad (4)$$

The four-photon element S_{eg} can be estimated from the relation $S_{eg} \sim Q_{eg}$, which changes into an equality under the same conditions as (3).

Hence, the second-order Raman resonance in the particle number is free from a linear Doppler effect and has a Lorentzian form with the forbidden transition halfwidth Γ.

As we found in Sect. 1, the stimulated absorption and emission of light at frequencies ω_1 and ω_2 excites the standing wave Raman oscillations at the frequency $2(\omega_1 - \omega_2) = \omega_{eg}$. The scattering of the light at the frequency ω_j $(j = 1, 2)$ on this standing wave is followed by emission at the Stokes and anti-Stokes frequencies

$$\omega_{jS} = \omega_j - \omega_{eg}, \quad \omega_{jaS} = \omega_j + \omega_{eg}.$$

The corresponding complex amplitudes of nonlinear polarization are

$$P_{jS}^{(5)} = E_j (E_1^* E_2)^2 \chi^{(5)}(2\omega_1 - 2\omega_2 - \omega_{eg}),$$
$$P_{jaS}^{(5)} = P_{jS}^{*(5)},$$

where $\chi^{(5)}(\omega)$ is the susceptibility tensor containing the Doppler-free resonance with the homogeneous width. A detailed description of the radiation resonances will be given in the subsequent paper.

3. Resonance in the Number of Particles for the $^3P_2^0 - {}^3P_0^0$ Neon Transition

In this section we estimate the rate of particle excitation (4) with neon as an example. Let us consider the initial g and final e levels to be the metastable neon levels $^3P_2^0$ (134041.8 cm^{-1}) and $^3P_0^0$ (134818.6 cm^{-1}), respectively. The Raman transition frequency is $\omega_{eg} = 776.8\ cm^{-1}$. The neon quantum transition $^3P_2^0 - {}^3P_0^0$ is of interest for us as it has a small broadening due to inelastic and dephasing collisions [6].

Since the resonance amplitude is proportional to the second power of the accuracy of the frequency coincidence of ω_1 with $\omega_{\alpha g}$ or ω_2 with $\omega_{\alpha e}$, we chose as an example ω_1 close to the $^3P_2^0 - {}^3D_1$ transition frequency $(\lambda_1 \approx \lambda_{\alpha g} = 6217.1$ Å) with an accuracy $\omega/\delta\omega \sim 10^5$ that yields $\omega_2 = \omega_1 - \omega_{eg}/2$ $(\lambda_2 = 6371.1$ Å). The intermediate level $\eta - {}^3P_1^0$ (134459.3 cm^{-1}) lies approximately halfway between g and e $(\omega_{\eta g} - \omega_{eg}/2 = 29.1\ cm^{-1} \ll \omega_{eg})$. Therefore the approximate expressions for Q_{eg} and S_{eg} given in Sects. 1 and 2 may be considered to be exact, i.e.

$$S_{eg} Q_{eg}^* = |Q_{eg}|^2 = [\omega_{\eta g} - (\omega_{eg}/2)]^{-2} \times |D_{e\eta}(\varepsilon_2^*, \omega_2 | \varepsilon_1) D_{\eta g}(\varepsilon_2^* | \omega_1, \varepsilon_1)|^2.$$

Let us consider the electromagnetic waves to be linearly polarized, $\varepsilon_1 = \varepsilon_2$. The line strengths for dipole transitions according to [7] are equal to $S(\alpha, g) = 2.27$, $S(\alpha, e) = 4.46$, $S(\alpha, \eta) = 12.4$ (a.u.). The calculations with

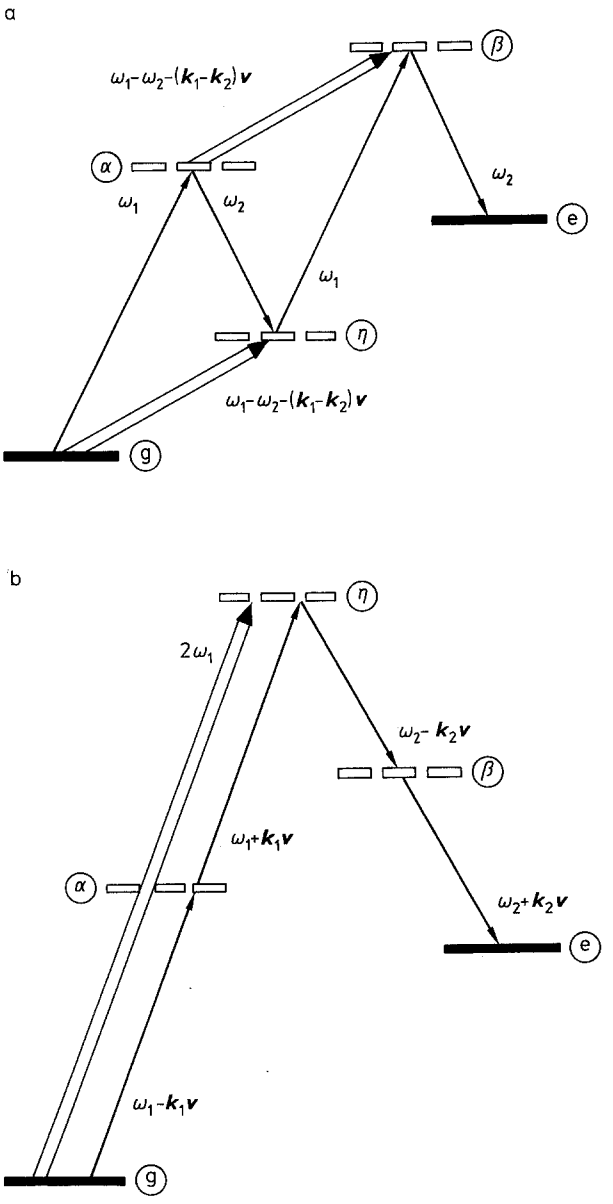

Fig. 1. Interactions exciting the Doppler-free Raman coherence ϱ_{eg}: the double SRS (a), and the stimulated absorption and emission of the pairs of counter-propagating photons (b). The double arrows show the Raman oscillations involved in the ϱ_{eg} excitation. The levels α and g (η) as well as β and e (η) are connected by dipole transitions. The η states are of the same parity as g and e

the level degeneracy yield the rate of excitation to the state e ($^3P_0^0$) in the center of the spectral line (4)

$$\dot{N}_e \approx 2.2 \times 10^{-24}\,\mathrm{s}^{-1} N_g I_1^2 I_2^2 \Gamma^{-1} \times \omega_{\alpha g}^2 (\omega_{\alpha g} - \omega_1)^{-2} \omega_{\alpha e}^2 (\omega_{\alpha e} - \omega_2)^{-2},$$

where the field intensities I_1, I_2 are in W/cm^2 and the homogeneous halfwidth Γ is in Hz.

The required laser radiation intensity may be obtained from this formula if the sensitivity threshold of the detecting scheme is known. Assuming $(\dot{N}_e)_{\mathrm{th}} = 1\,\mathrm{s}^{-1}\,\mathrm{cm}^{-3}$ we obtain the threshold value of the light intensity

$$I_{\mathrm{th}} \sim 10\,\mathrm{W\,cm}^{-2} [(\Gamma/P)(\delta\omega/\omega)^2]^{1/4},$$

where P is the pressure in Torr.

According to [8], $\Gamma/P = 2$ MHz/Torr, then with $\omega/\delta\omega \sim 10^5$ the estimate yields $I_{\mathrm{th}} \sim 1$ W/cm^2, and with $I > I_{\mathrm{th}}$ the excitation rate is $\dot{N}_e \sim I^4\,\mathrm{s}^{-1}\,\mathrm{cm}^{-3}$. This estimate may be used for other atoms and molecules as well.

4. Conclusion

We have suggested the occurrence of Doppler-free resonances of atomic or molecular interactions with two standing optical waves, whose frequency difference is equal to half the Raman transition frequency. These resonances are caused by the second-order stimulated Raman scattering and by complete compensation of Doppler shifts in each scattering event. The considered method allows us to investigate the visible, IR and FIR forbidden atomic and molecular transitions, which obey the total angular momentum selection rules $\Delta J = 0, \pm 2, \pm 4$, by visible and UV laser radiation and with higher resolution than is achieved in the well-known laser spectroscopy methods of Raman light scattering.

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